

AD-A222 643

DTIC FILE COPY

2

OFFICE OF NAVAL RESEARCH

Contract N00014-88-K-0305

Technical Report No. 21

Catalytic Synthesis of Polymethylsilsesquioxanes

Richard M. Laine, Jeffrey A. Rahn, Kay A. Youngdahl, John F. Harrod,

To be published in

Am. Chem. Soc. Symp. Series in press

paper presented at the Am. Chem. Soc. Meeting; April 1990, Boston,
MA. Catalysis Secretariat

Department of Materials Science and Engineering

University of Washington

Roberts Hall, FB-10

Seattle, WA 98195



Reproduction in whole or in part is permitted
for any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1d. RESTRICTIVE MARKINGS										
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release Distribution unlimited										
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE												
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report 21		5. MONITORING ORGANIZATION REPORT NUMBER(S)										
6a. NAME OF PERFORMING ORGANIZATION University of Washington	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION										
6c. ADDRESS (City, State, and ZIP Code) Dept. of Materials Science & Engineering Roberts Hall, FB-10 Seattle, WA 98105		7b. ADDRESS (City, State, and ZIP Code) Office of Naval Research Dept. of the Navy, 800 N. Quincy Arlington, VA 22217										
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-88-K-0305										
8c. ADDRESS (City, State, and ZIP Code) Office of Naval Research 800 N. Quincy Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS <table border="1"><tr><td>PROGRAM ELEMENT NO. N0014-88</td><td>PROJECT NO. K-305</td><td>TASK NO.</td><td>WORK UNIT ACCESSION NO</td></tr></table>		PROGRAM ELEMENT NO. N0014-88	PROJECT NO. K-305	TASK NO.	WORK UNIT ACCESSION NO					
PROGRAM ELEMENT NO. N0014-88	PROJECT NO. K-305	TASK NO.	WORK UNIT ACCESSION NO									
11. TITLE (Include Security Classification) Catalytic Synthesis of Polymethylsilsesquioxanes												
12. PERSONAL AUTHOR(S) Richard M. Laine, Jeffrey A. Rahn, Kay A. Youngdahl, John F. Harrod												
13a. TYPE OF REPORT Publication	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) May 31, 1990	15. PAGE COUNT									
16. SUPPLEMENTARY NOTATION												
17. COSATI CODES <table border="1"><tr><th>FIELD</th><th>GROUP</th><th>SUB-GROUP</th></tr><tr><td> </td><td> </td><td> </td></tr><tr><td> </td><td> </td><td> </td></tr></table>		FIELD	GROUP	SUB-GROUP							18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP										
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Dimethyltitanocene, Cp_2TiMe_2 , where $Cp = C_5H_5$, can be used to promote the redistribution of $-(MeHSiO)_x$ -cyclomers and linear oligomers to produce a polymethylsilsesquioxane copolymer of the type $-(MeHSiO)_0.3 \{MeSi(O)_{1.5} \}_{0.7}$. A mechanism for this redistribution is suggested, that involves σ -bond metathesis promoted by a Ti(IV) species. The structural evolution of the polymethylsilsesquioxane copolymer as it is heated to 1000°C is followed using solid state ^{29}Si NMR. TGA experiments and chemical analysis support the NMR results which indicate that most of the starting monomer is either volatilized or undergoes further redistribution, so that by 400°C only polymethylsilsesquioxane remains. The active catalyst derived from Cp_2TiMe_2 will also catalyze the alcoholysis of the Si-H bonds in the copolymer producing alkoxy derivates, $-(Me(R)SiO)_{0.3} \{MeSi(O)_{1.5}\}_{0.7}$ ($R = Me, Et, nPr, nBu$). This same catalyst system can be used to polymerize polysilazane oligomers such as $-(MeHSiNH)_x$ - or $-(H_2SiNMe)_x$ -, but only if some $-(MeHSiO)_x$ - is present. The ceramic yields of 1:1, 1:3, 1:9, and 1:18 ratios of $-(MeHSiO)_x$ - : $-(MeHSiNH)_x$ - were much higher than that found for the pure polysilazane.												
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION										
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL									

Catalytic Synthesis of Polymethylsilsesquioxanes

Richard M. Laine,* Jeffrey A. Rahn, Kay A. Youngdahl and John F. Harrod†
Contribution from the Department of Materials Science and Engineering
University of Washington, Seattle, WA 98195 and, the †Department of
Chemistry, McGill University, Montreal, Canada

Abstract:

Dimethyltitanocene, Cp_2TiMe_2 , where $\text{Cp} = \text{C}_5\text{H}_5$, can be used to promote the redistribution of $-\text{[MeHSiO]}_x-$ cyclomers and linear oligomers to produce a polymethylsilsesquioxane copolymer of the type $-\text{[MeHSiO]}_{0.3}[\text{MeSi(O)}_{1.5}]_{0.7}-$.

A mechanism for this redistribution is suggested, that involves σ -bond metathesis promoted by a Ti(IV) species. The structural evolution of the polymethylsilsesquioxane copolymer as it is heated to 1000 °C is followed using solid state ^{29}Si NMR. TGA experiments and chemical analysis support the NMR results which indicate that most of the starting monomer is either volatilized or undergoes further redistribution, so that by 400 °C only polymethylsilsesquioxane remains.

The active catalyst derived from Cp_2TiMe_2 will also catalyze the alcoholysis of the Si-H bonds in the copolymer producing alkoxy derivates, $-\text{[Me(RO)SiO]}_{0.3}[\text{MeSi(O)}_{1.5}]_{0.7}-$ ($\text{R} = \text{Me, Et, nPr, nBu}$). This same catalyst system can be used to polymerize polysilazane oligomers such as $-\text{[MeHSiNH]}_x-$ or $-\text{[H}_2\text{SiNMe]}_x-$, but only if some $-\text{[MeHSiO]}_x-$ is present. The ceramic yields of 1:1, 1:3, 1:9, and 1:18 ratios of $-\text{[MeHSiO]}_x-\text{:}[\text{MeHSiNH}]}_x-$ were much higher than that found for the pure polysilazane. At higher ratios of polysilazane, the apparent ceramic composition was the same as that found for the pure polysilazane.

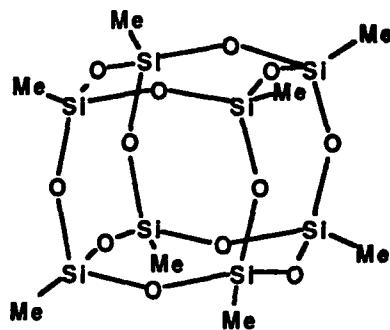
Accession For	
NTIS	CP&I
DTIC	TIB
U.S. Govt. 1	<input checked="" type="checkbox"/>
Justification	<input type="checkbox"/>
Date	
Distribution	
Classification	
Subject	
Notes	

A-1



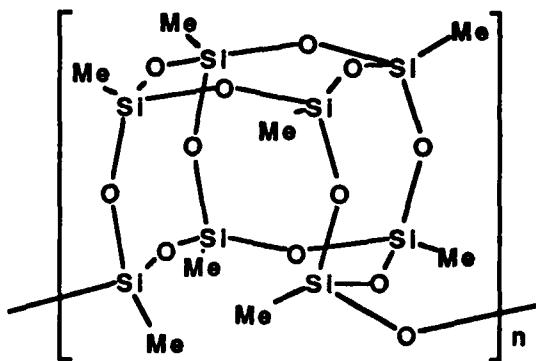
Introduction

Silsesquioxanes, $\text{RSi(O)}_{1.5}$, represent a unique and poorly studied subset of polyalkylsiloxanes. This is despite the fact that they offer many exceptional properties. For example, silsesquioxanes, because of their need to form three Si-O-Si bonds, assume regular polyhedral shapes such as shown for octamethyloctasilsesquioxane:¹



These polyhedral shapes have geometries very similar to those found for silica and its derivatives. Feher et al² have used this similarity as the basis for developing molecular models of silica surfaces. The regular geometry also contributes to such properties as high temperature stability¹ and high hardness.³ Octamethyloctasilsesquioxane is stable in air to 415°C at which temperature it sublimes.

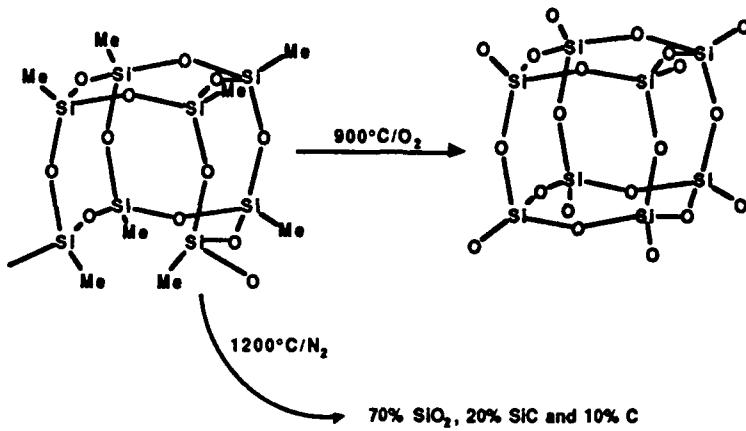
Polysilisesquioxanes appear to have cage rather than ladder structures,⁴ wherein the polymer is formed by opening of a polyhedral edge as suggested for polymethylsilsesquioxane:



Polymethylsilsesquioxane, $[\text{MeSi(O)}_{1.5}]_x$, is stable in air to temperatures >500°C and, as we will show below, to at least 600°C in nitrogen. The phenyl derivative is reported to be stable to temperatures of

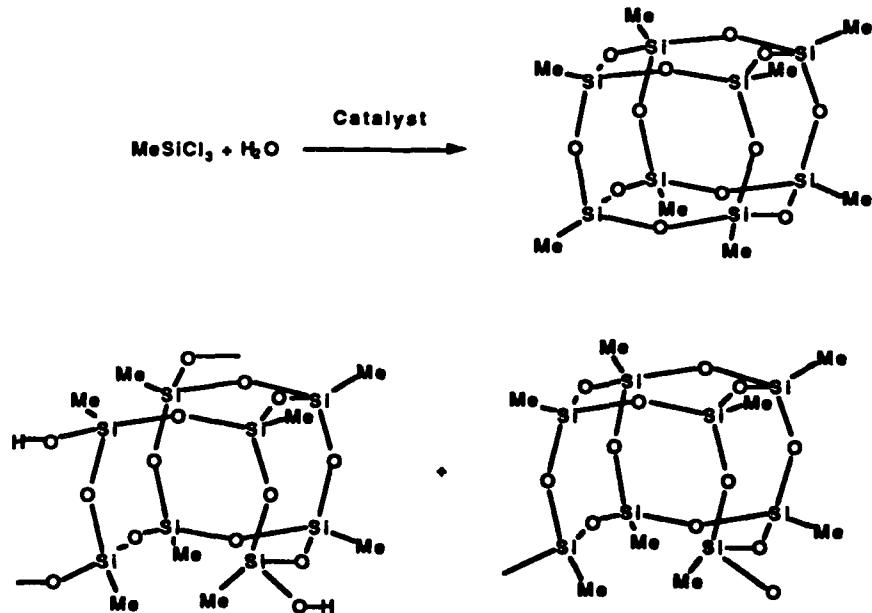
800°C.¹ The cage structure has been suggested to be useful for making microporous materials.⁵

Polymethylsilsesquioxanes have been used as protective polymer coatings in the electronics industry⁶ and as precursors to silica and SiO_{4-x}C_x glasses:⁷



From an engineering standpoint, these materials offer exceptional properties that should lead to widespread applications. Unfortunately, their propensity for forming gels makes it extremely difficult to prepare useful, processable quantities of any given material.

Until recently, the only method of preparing silsesquioxanes was via hydrolysis of the alkyltrichloro or trialkoxysilane:^{1,2,5}



Separation of the polyhedral or polyalkylsilsesquioxane from the reaction mixture is extremely difficult and the isolable yields for these compounds are quite poor, typically ranging from 15-30%. Consequently, the discovery by one of us that titanium will catalyze the redistribution of alkoxy silanes under extremely mild conditions, reaction (1),⁸ suggested that



it might be possible to synthesize polysilsesquioxanes via a similar route which eliminates the need for a hydrolytic synthesis:



This reaction works very effectively and we present here an overview of our recent efforts to prepare and characterize the resulting polymers and their properties. The work presented here includes work previously published elsewhere.^{9,10}

Results and Discussion:

Neat mixtures of either cyclic $-\text{[MeHSiO]}_n-$ ($n = 4, 5$), or linear oligomeric, $\text{Me}_3\text{Si}-\text{[MeHSiO]}_n-\text{H}$ ($M_n \sim 2000$ D) with 0.2 mol % $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiMe}_2$ will turn royal blue (under N_2 at 20°C) following an induction period of ca. 15 min. MeSiH_3 is evolved rapidly with stirring and in 5-7 min the solution becomes extremely viscous and gels in 10-15 min. Solid state ^{29}Si NMR (see below) indicates that the final gel consists of a copolymer of approximate composition $-\text{[MeHSiO]}_{0.3}[\text{MeSi(O)}_{1.5}]_{0.7}-$. The induction period that precedes reaction appears to be related to free radical promoted decomposition of $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiMe}_2$ which generates the true catalyst.

Soluble product can be obtained by dilution with toluene. Thus, reaction in a five-fold excess (with respect to added $-\text{[MeHSiO]}_n-$) of toluene gives a stable solution after 72 h of reaction. Reactions attempted with less than a five-fold excess of toluene lead inevitably to the formation of a gel.

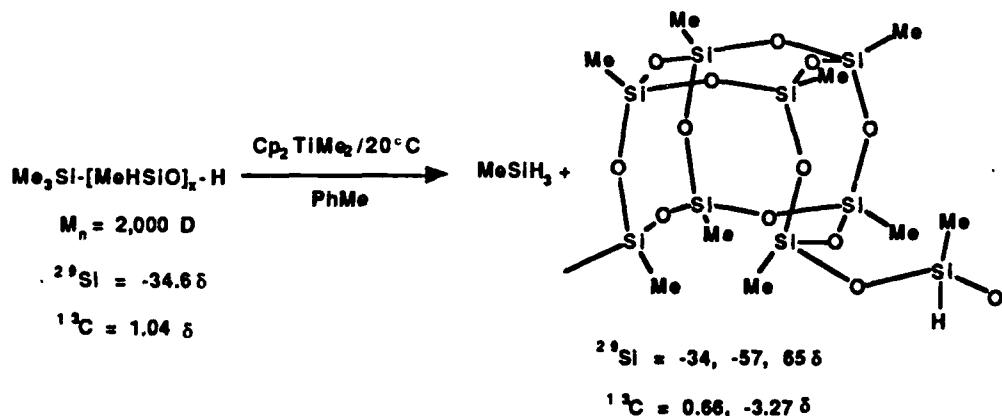
Thin films cast from the resulting copolymer/toluene solution exhibit moderate elastomeric properties, excellent adhesion to glass, carbon, and metal surfaces and, can be heated without significant changes in properties to 250°C . Above this temperature, the polymer becomes more and more

brittle; however, no visible degradation occurs up to temperatures of approximately 400°C. However, solid state ^{29}Si NMR can be used to demonstrate that structural changes do occur on heating.

Because of our continuing interest in polymer precursors to ceramics we followed the structural evolution of the $\text{Me}_3\text{Si}-[\text{MeHSiO}]_n-\text{H}$ derived copolymer during heating to 1000°C using solid state ^{29}Si NMR (Figure 1). At room temperature, we see the Me_3Si (3%) and $\text{Me}(\text{OH})\text{Si}$ (4%) end caps of the original oligomer together with peaks for $-\text{[MeHSiO]}_n-$ (30%) and $-[\text{MeSi(O)}_{1.5}]_x-$ (70%). TGA experiments and chemical analysis⁹ support the NMR results which indicate that most of the starting monomer is either volatilized or undergoes further redistribution such that by 400°C only the pure polymethylsilsesquioxane remains. Note that in the NMR the sharp singlet of the $[\text{MeSi(O)}_{1.5}]$ silicon is present at 600°C but becomes severely broadened as the polymer is transformed into a glass at 800°C.¹⁰

Insert Figure 1

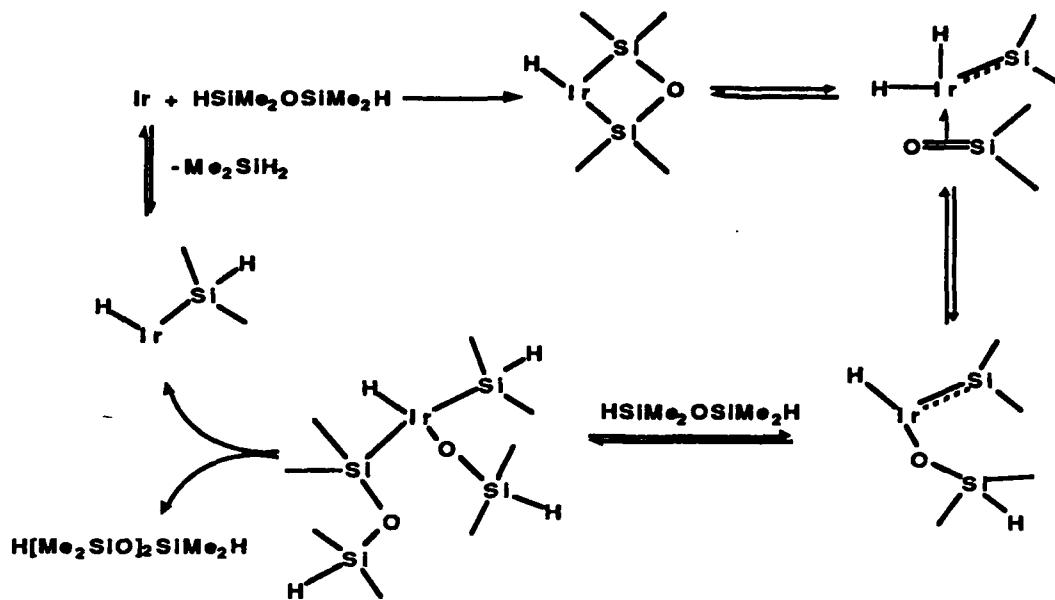
Nearly identical copolymer compositions are obtained from the copolymer generated in toluene as determined following solvent removal. The NMR established composition is confirmed by the chemical analysis.¹¹ Given the relatively simple ^{29}Si NMR, the copolymer structure is assumed to be that shown below:



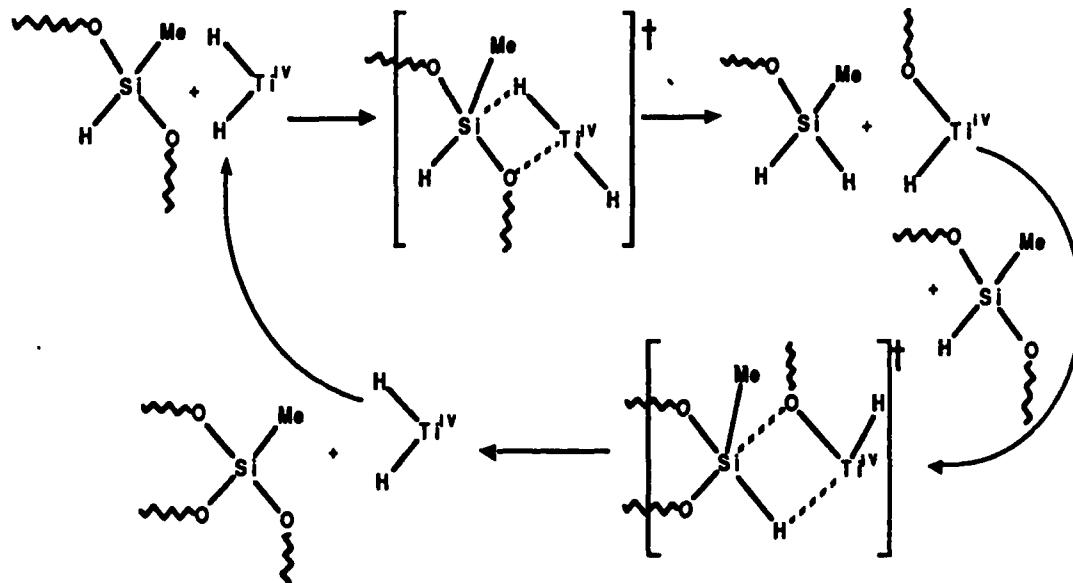
However, it is possible that other polyhedral silsesquioxane structural units also form in the copolymer.

Catalytic redistribution of hydridosiloxanes by transition metals was first reported by Curtis and Epstein.¹² They discovered that iridium complexes promoted redistribution of $\text{H}-[\text{Me}_2\text{SiO}]_x-\text{SiMe}_2\text{H}$ and proposed the

following type of mechanism:

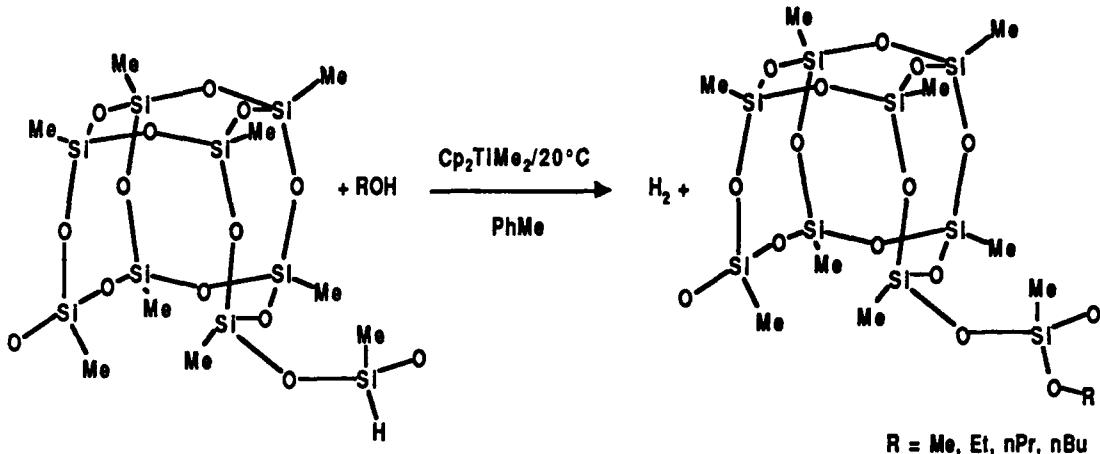


Based on recent work by Tilley et al¹³ on the reactions of d° metals with silanes, we believe that a different mechanism is operating here. This mechanism probably involves σ-bond metathesis promoted by a Ti (IV) species generated by decomposition of $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiMe}_2$. The following mechanism is suggested based on the work of Tilley et al; however, substantiation must await detailed kinetic studies.



We propose a Ti (IV) catalytic process despite the royal blue color of the reaction which is typical Ti (III) compounds and despite our having isolated Ti (III) complexes¹⁴ in related systems because of the following discovery.

Because the copolymer $-[\text{MeHSiO}]_{0.3}[\text{MeSi(O)}_{1.5}]_{0.7}-$ still retains Si-H groups which are susceptible to further modification either by hydrosilylation or alcoholysis, we explored the possibility of changing the copolymer rheological characteristics by reaction with alcohols. We find that addition of alcohols to the toluene reaction solution anytime during the course of reaction leads to very effective alcoholysis of the copolymer:



The addition of MeOH leads to a rapid color change from royal blue to yellow orange and extremely rapid (almost violent) evolution of hydrogen. The reaction is complete within the time of addition. The other alcohols are less reactive, with the n-BuOH reaction taking 1-2 days at room temperature.

Once solvent is removed, the methoxy derivative will become gel-like in hours to days depending on the temperature of the room. The n-butoxy derivative in contrast is much less susceptible to gelling and will remain as a viscous liquid for periods up to one week. N-propanol solutions of the n-propoxy derivative (25 wt %) will remain stable almost indefinitely. NMR characterization indicates the formation of $-[\text{Me}(\text{RO})\text{SiO}]_{0.3}[\text{MeSi(O)}_{1.5}]_{0.7}-$ and confirms the initial copolymer composition.¹⁰ These polymers are actually a masked form of $-[\text{MeSi(O)}_{1.5}]_x-$ given that addition of water will lead to hydrolysis of the SiOR bond and water can actually be used to cause thermosetting!

The yellow-orange color is typical of a Ti (IV) catalyst and when coupled with Tilley's work suggests the above proposed Ti (IV) promoted redistribution reaction.

Polysilazane Polymerizations¹⁵

The success of this catalyst system suggested that it might also be used

for the catalytic polymerization of polysilazane oligomers such as $-[\text{MeHSiNH}]_x$ - or $-[\text{H}_2\text{SiNMe}]_x$ - . This would offer an alternative to the ruthenium catalysts that we have previously used to form tractable silicon nitride preceramic polymers. To our surprise, neither oligomer underwent catalytic redistribution when mixed with $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiMe}_2$ despite the fact that the catalyst reacted and some small amount of gas (presumably CH_4) evolved coincident with reaction.

This result was disappointing; however, we attempted to catalyze the redistribution of $-[\text{MeHSiO}]_x$ - in the presence of $-[\text{MeHSiNH}]_x$ - to explore the possibility of trapping the $-[\text{MeHSiNH}]_x$ - oligomer in the resulting silsesquioxane gel. We used ceramic yield as a measure of our success. Thus, Figure 2 shows TGAs for the copolymer derived from $-[\text{MeHSiO}]_x$ - (74-78% ceramic yield at 900°C in N_2), pure $-[\text{MeHSiNH}]_x$ - (37% ceramic yield at 900°C in N_2) and a 1:1 mixture of $-[\text{MeHSiO}]_x$ -/- $-[\text{MeHSiNH}]_x$ - . If the 1:1 mixture were to act simply as a physical mixture, then the ceramic yields for the combination should be the arithmetic mean or 56%. Instead, we find that (see Figure 2) the ceramic yield is $\approx 72\%$. This would suggest that we were successful in trapping the silazane in the interstices of the polymethylsilsesquioxane gel. However, an alternate explanation is that in the presence of the hydridosiloxane, the catalyst is now capable of catalyzing redistribution of polysilazanes. To test this, we changed the siloxane:silazane ratio. Table 1 shows both that as the ratio is changed from 1:1 to 1:3 to 1:18 reaction continues to occur, the ceramic yields stay high (relative to pure polysilazane) and the resulting ceramic products begin to look as like the ceramic products obtained from pure $-[\text{MeHSiNH}]_x$ - . Our preliminary conclusion is that titanium catalyzed redistribution of $-[\text{MeHSiNH}]_x$ - requires the presence of some quantity of hydridosiloxane as cocatalyst.¹⁵

It is important to note here that the apparent compositions reported in Table 1 are a form of book-keeping that is not truly indicative of the actual nature of the $\text{SO}_{4-x}\text{C}_x$ glass.⁹ However, these compositions are adequate for describing the selectivity to ceramic products, at 900°C, obtained by pyrolysis of $-[\text{MeHSiNH}]_x$ - and $-[\text{H}_2\text{SiNMe}]_x$ - . The siloxane/silazane mixtures are perhaps better treated as mixtures of silicon oxynitride, Si_2ON_2 and $\text{SO}_{4-x}\text{C}_x$ or Si_2ON_2 and silicon nitride/carbide depending on the percentage of initial hydridosiloxane.

<u>Compound</u>	<u>Ceramic Yield</u>	<u>Apparent Ceramic Composition</u>		
		<u>Si₃N₄</u>	<u>SiC</u>	<u>C(x's)</u>
MeHSiNH	65	64	25	10
H ₂ SiNMe	63	75	--	18
MeHSiO	78	70 SiO ₂	20	10
1:1 MeHSiO/MeHSiNH	72	31	20	10
1:3 MeHSiO/MeHSiNH	64	43	20	10
1:9 MeHSiO/MeHSiNH	64	53	22	10
1:18 MeHSiO/MeHSiNH	63	62	19	11

Table 1. Apparent Ceramic Compositions for Selected Polysilazanes, Polymethylsilsesquioxane and Various Mixtures Pyrolyzed to 900°C in Nitrogen. Heating rate 5°C/min. Apparent ceramic compositions are calculated assuming Si is the limiting element. N is the limiting element when -[H₂SiNMe]_x- is the preceramic.

Conclusions

Titanium catalyzed redistribution of -[MeHSiO]_x- provides a useful route to tractable, processable methylhydridosiloxane-methylsilsesquioxane copolymers. The "Ti" catalyst active in the redistribution reaction will also promote alcoholysis of the resultant copolymers to produce alkoxy derivatives which display equivalent or slightly better, high temperature stability than the starting copolymer and more controllable rheology.

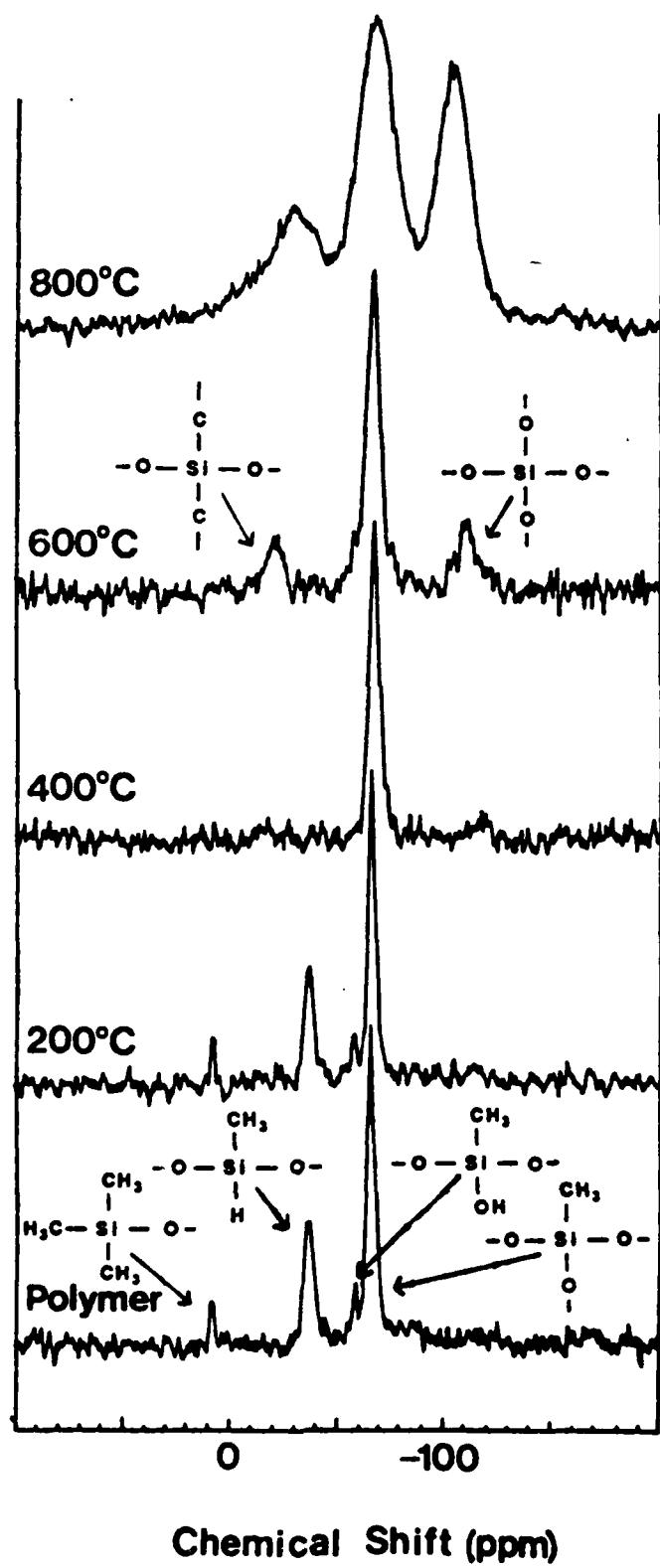
Although Cp₂TiMe₂ will not catalyze the polymerization of pure -[MeHSiNH]_x-, in the presence of small amounts of hydridosiloxane, it is an active catalyst precursor and permits catalytic redistribution that leads to a high ceramic yield silicon nitride precursor.

Acknowledgements

We would like to thank the Strategic Defense Sciences Office through the Office of Naval Research for support through ONR contract No. NOOO14-88-K-0305. RML would like to thank IBM Corp. for partial support of this work. RML and JFH thank NATO for a travel grant.

References

1. Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199.
2. (a) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741. (b) Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3850.
3. From data sheet on GE Polyalkylsilsesquioxane (PALS) coatings distributed by General Electric Company.
4. Frye, C. L.; Klosowski, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 4599.
5. Shea, K. J.; Loy, D. A. *Chem. Mat.* **1989**, *1*, 572.
6. January, J. R. U.S. Patent 4,472,510.
7. (a) White, D. A.; Oleff, S. M.; Boyer, R. D.; Budringer, P. A.; Fox, J. R. *Adv. Cer. Mat.* **1987**, *2*, 45. (b) White, D. A.; Oleff, S. M.; Fox, J. R. *Adv. Cer. Mat.* **1987**, *2*, 53. (c) Baney, R. In *Ultrastructure Processing of Ceramics, Glasses, and Composites*; Wiley and Sons: New York, 1983; pp 245-255.
8. Harrod, J. F.; Xin, S.; Aitken, C.; Mu, Y.; Samuel, E. Presented at the International Conference on Silicon Chemistry, St. Louis, MO, June 1986.
9. Rahn, J. A.; Laine, R. M.; Zhang, Z. F., Proceedings of the Materials Research Society Symposium on "Polymer Based Molecular Composites" Boston, Dec. 1989, in press.
10. Laine, R. M.; Youngdahl, K. A.; Babonneau, F.; Hoppe, M. L.; Zhang, Z. F.; Harrod, J. F., submitted for publication in *Chem. Mat.*
11. Found C = 19.4%, H = 5.4%, Si = 41.5%, Calc. for $[\text{MeHSiO}]_{0.3}[\text{MeSi(O)}_{1.5}]_{0.7}$. C = 18.5%, H = 5.1%, Si = 43.1%
12. Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.
13. Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.*, **1989**, *110*, 3757.
14. Harrod, J. F.; in *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*, NATO ASI Ser. E: Appl. Sci.-No. 141; Laine, R. M. Ed.; Martinus Nijhoff Publ., Amsterdam **1988**, p 103.
15. Youngdahl, K. A.; Hoppe, M. L.; Laine, R. M.; Harrod, J. F. *Proceedings of the 3rd International Conference on Ultrastructure of Ceramics, Glasses, and Composites*; Uhlmann, D.; Ulrich, D. R., Eds.; in press.



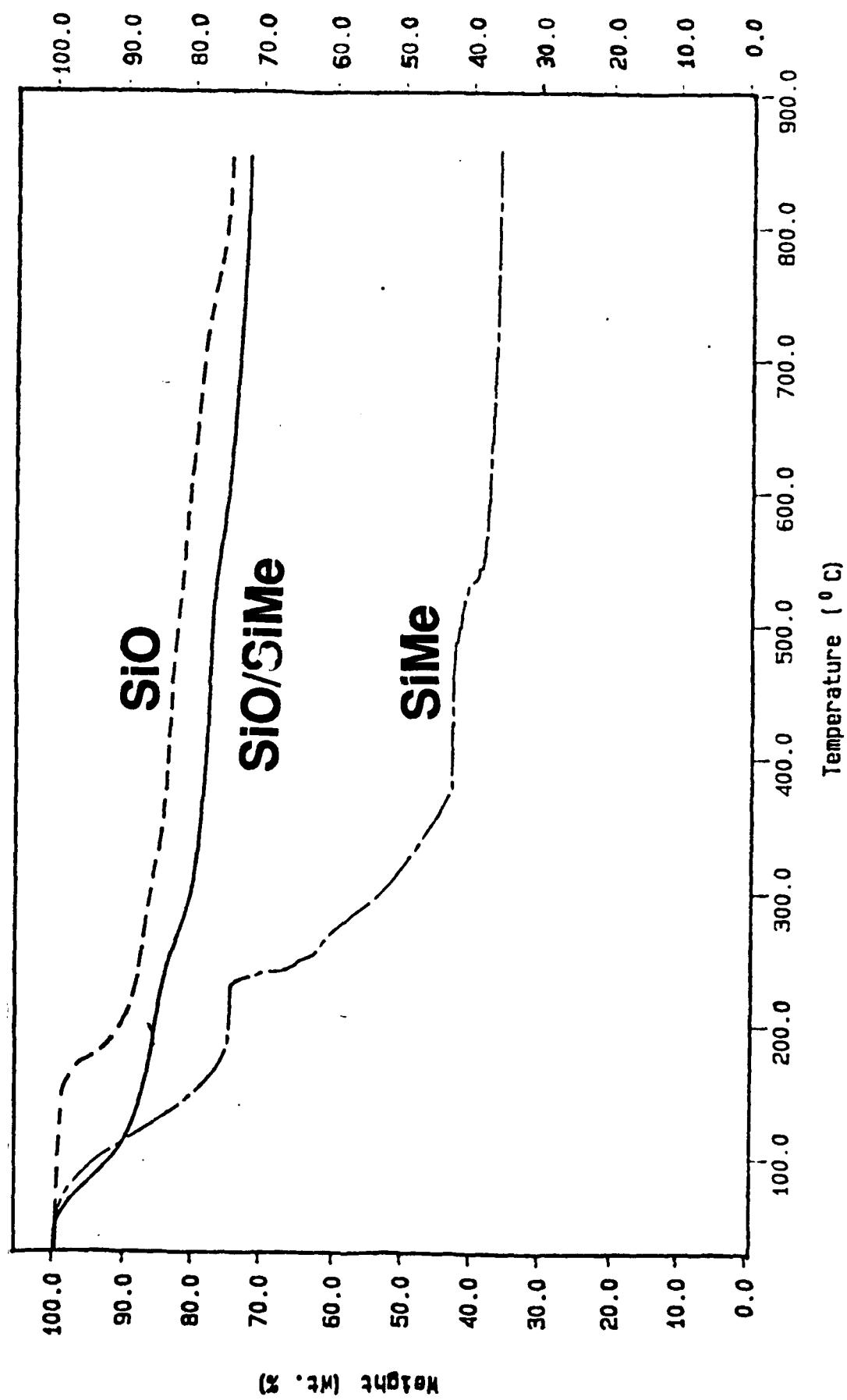


Figure 1. Chemical evolution of $\text{Me}_3\text{Si}-[\text{MeHSiO}]_n-\text{H}$ derived copolymer during heating to selected temperatures 1000 °C using solid state ^{29}Si NMR. M = Me_3SiO ; D = $\text{Me}_2\text{Si}(\text{O})_2$; DH = $\text{MeHSi}(\text{O})_2$; DOH = MeSi(OH)(O)_2 ; T = $\text{MeSi}(\text{O})_3$; and Q = $\text{Si}(\text{O})_4$.

Figure 2. Thermogravimetric Analysis of $-[\text{MeSi}(\text{O})_{1.5}]x-$ (a), $-[\text{MeHSiNH}]x-$ (c), and a 1:1 Copolymer of $-[\text{MeHSiNH}]x-$ and $-[\text{MeSi}(\text{O})_{1.5}]x-$ (b). Pyrolyzed under N_2 at a heating rate of 5 °C /min.